Tunnel diodes fabricated from CdSe nanocrystal monolayers

S.-H. Kim, G. Markovich, and S. Rezvani
Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569

S. H. Choi and K. L. Wang
Department of Electrical Engineering, University of California at Los Angeles, Los Angeles, California 90095-1569

J. R. Heath[a)]
Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569

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A parallel approach for fabricating nanocrystal-based semiconductor–insulator–metal tunnel diodes is presented. The devices consisted of a Au electrode, a monolayer of 38 Å CdSe nanocrystals, an insulating bilayer of eicosanoic acid ($C_{19}H_{39}CO_2H$), and an Al electrode. Each device was approximately 100 μm^2. Conductance measurements at 77 K reveal strong diode behavior and evidence of Coulomb blockade and staircase structure. A single barrier model was found to reproduce the electronic characteristics of these devices. © *1999 American Institute of Physics.* [S0003-6951(99)04502-7]

The unique chemical and size-dependent properties of nanocrystals (NCs) have made them attractive candidates as electronic and photonic materials. Relatively straightforward fabrication procedures have been reported for certain NC-based devices, such as light-emitting diodes,[1] photovoltaics,[2] and capacitors.[3] Other devices, however, such as single-electron transistors[4] and single-electron tunnel junctions,[5] require two electrical contacts to a single particle, and are hard to fabricate.[6] The difficulty arises not just because of the length scales involved, but also because chemically fabricated NCs are unstable toward many electronic materials processing technologies. In this letter, we present a parallel fabrication technique for the construction of CdSe nanocrystal-based metal–insulator–semiconductor (MIS) tunnel diodes. The key component that allows for top and bottom contacts to the nanocrystal (mono) layer is a molecularly thin insulating layer of eicosanoic acid, prepared as a Langmuir–Blodgett (LB) film. Strong diode behavior and a series of single-electron charging states, characterize the conductance of the devices. A standard model for MIS devices,[7] modified to include the finite-size characteristics of the NCs, successfully reproduced the measured conductance of the diodes.

Figure 1(a) shows a cross sectional view of the device. It consists of a Au electrode, NC monolayer, molecular insulator, and a top Al electrode. The structure resembles a normal metal–insulator–semiconductor diode, in which a CdSe NC monolayer[8] replaces the semiconductor, and a molecular (LB) film replaces what is, typically, an oxide tunnel barrier.

Other groups have investigated the insulating behavior of LB films of organic amphiphiles in sandwich-structure devices.[9,10] Because of defects in the LB film, it is necessary to transfer several monolayers to fabricate what are, effectively, single-monolayer devices. We found that, for ~100 μm^2 devices, 6 LB monolayers of eicosanoic acid gave an ''effective'' insulating layer of 2–3 nm (about 1 ML), and a device resistance of ~10 MΩ.

38±4 Å CdSe NCs were synthesized according to literature recipes,[11] ligand-exchanged with hexanethiol, and characterized by UV/vis absorption spectroscopy and x-ray powder diffraction. A particle/$HCCl_3$ solution was spread on the

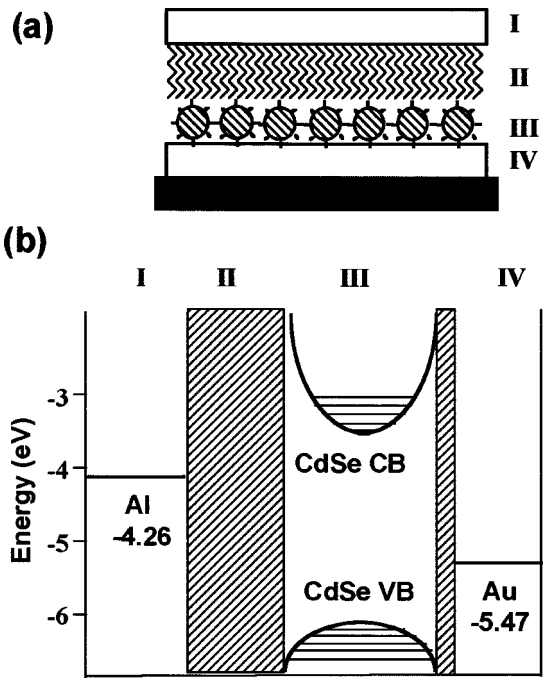

FIG. 1. Cross-sectional diagram (a) and energy-level diagram (b) of the CdSe nanocrystal-based MIS diode. The labeled regions, in either diagram, correspond to: (I) an aluminum electrode; (II) a Langmuir–Blodgett monolayer of eicosanoic acid; (III) a single monolayer of 38 Å CdSe nanocrystals; and (IV) a gold electrode patterned on a SiO_2 substrate. The thin tunnel barrier between the CdSe nanocrystals and the gold electrode corresponds to the hexanethiol surface passivants on the nanocrystal surfaces. The energy scale in (b) is relative to the vacuum level.

a)Corresponding author; electronic mail: heath@chem.ucla.edu

water surface of a Langmuir trough. The film was compressed to an area of 1600 $Å^2$/NC, and transferred as a single- monolayer Langmuir–Schaeffer (LS) film to a substrate [1500 Å SiO_2 on Si(100)] patterned with 4 μm wide Au electrodes, or to an amorphous carbon coated transmission electron microscope grid for microscopy. Six monolayers of eicosanoic acid (19 $Å^2$/molecule) were then transferred as LB films. The upper Al electrode, oriented perpendicular to the Au electrode, was then evaporated through a 20–50 μm slit, to produce a several devices with active areas of 80–200 μm^2.

After device construction, the device was connected to the measuring circuit for both ambient and 77 K measurements. Current/voltage, and conductance/voltage measurements were carried out, producing consistent results. For the conductance measurements, a 50 $mV_{p\text{-}p}$ amplitude sinusoidal wave floating on a tunable dc offset was applied across the circuit, and conductance was measured with lock-in detection. We also measured conductance with an impedance analyzer and obtained identical results.

The energy level diagram of the device is presented in Fig. 1(b). We estimate the conduction-band (CB) edge of the CdSe particles to be -4.0 eV from the electron affinity and ionization potential of bulk CdSe,[12] with a correction for the quantum size effect.[13] The valence-band (VB) location is calculated from the CB edge and the measured band gap. The tunneling barrier between the NCs and the Al electrode dominates the electrical characteristics of the device. We thus approximate the device as a (single-barrier) MIS tunnel diode. The eicosanoic acid LB film is approximated as a monolayer (25 Å width). This barrier is thick enough that we do not expect any alignment of energy levels between the Al electrode and the NC monolayer.

We set up a model to derive the tunneling characteristics of this device. Depending on the applied bias, a charge carrier can tunnel from the Al electrode to empty CdSe CB states, or from the CdSe VB to empty aluminum states. The current can be express by the Golden rule:[7]

$$I=\int_{-\infty}^{\infty} T(E)\,\eta_m(E)\,\eta_s(E)[F_m(E)-F_s(E)]dE. \qquad (1)$$

In Eq. (1), $T(E)$ is the tunneling probability between two levels, $\eta_{m\text{ or }s}(E)$ is the density of states (DOS) of the metal or semiconductor, and $F_{m\text{ or }s}$ is the Fermi-distribution function. For experiments carried out at 77 K, we neglect $F_{m\text{ or }s}$. Also, in Eq. (1) we neglect the transverse energy-loss factor. In Fig. 2(a), we graphically represent the tunneling between the CB of the CdSe NCs and the Al electrode. Here, the electrons between the dashed lines can only tunnel to the semiconductor side. This limits the integral range of (1) from the bottom of the CdSe CB band to the Fermi level of the metal. With an applied bias, the conductance (dI/dV) becomes

$$dI/dV(V)=T(E_f^0+qV)\,\eta_m(E_f^0+qV)\,\eta_s(E_f^0+qV), \qquad (2)$$

where E_f^0 is the Fermi level of the Al with zero bias, q is the electron charge, and V is the applied voltage. From the WKB approximation, the tunneling probability can be approximated as $T(E)\approx\exp(-2\int_{x1}^{x2}k(x)dx)\approx\exp(-2kd)$.[7] We used a parabolic approximation to estimate the DOS of the Al electrode and CdSe NC layers, resulting in a $E^{1/2}$ dependency on the DOS. However, the small size of the CdSe particles implies the presence of (Coulombic) charging energy states in addition to the DOS of the particles. Taking into account the size distribution of the particles, we can express the DOS of the CdSe particles as[14]

$$\eta_s=\eta_s^0\sum_{n=0}^{\infty}\frac{\exp[-(E-nE_c)^2/2\sigma^2]}{\sqrt{2\pi\sigma^2}}, \qquad (3)$$

where η_s is the DOS of the particles, η_s^0 is the DOS without the charging states, E_c is the charging energy, and σ is the size-dependent standard deviation in energy space. In Fig. 2(b) we present our measured (77 K) and calculated conductance curves. For negative biases no current was measured up to an applied voltage of -2 V. For a series of separately fabricated devices using same-size CdSe particles, we observed variances in the shape of the dI/dV characteristics. However, the diode behavior, the onset of current flow, and the first peak positions were all consistent. For diodes fabricated from larger particles, the first peak in the conductance measurement was observed to shift to lower voltages.

The simulated conductance plot matches the experiment if we assign the E_c a value of 210 ± 30 meV, and the CB edge to be -3.6 eV. E_c of an isolated 38 Å particle is 290 meV. If the particle is in close proximity to a metal electrode

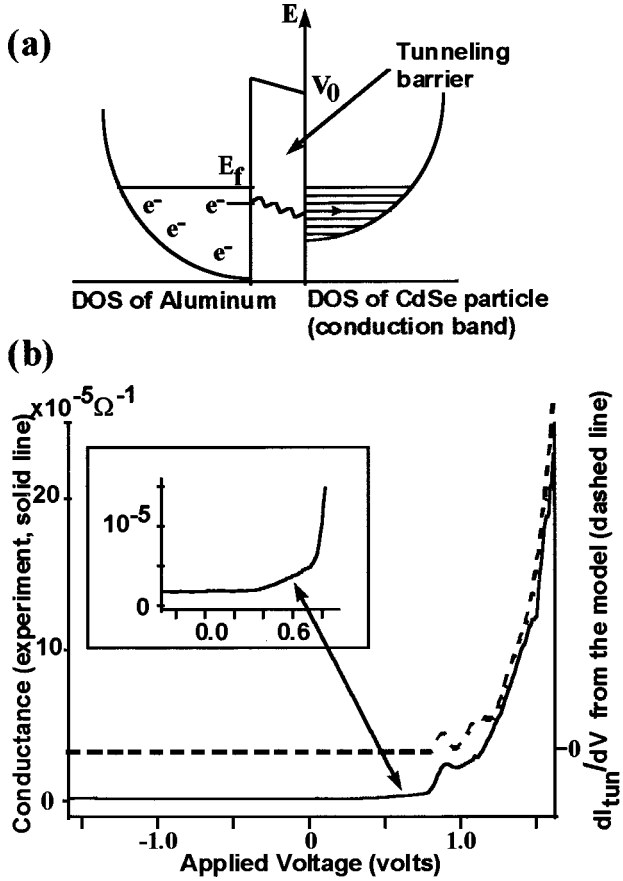

FIG. 2. (a) The single-barrier model utilized to calculate the electrical characteristics of the nanocrystal-based MIS diodes. With a particular applied bias voltage, electrons can tunnel between the Al electrode and the CdSe conduction band. The reverse process (from the CdSe valence band to the Al electrode) requires an applied bias in excess of -2 V. (b) The measured (solid line) and calculated (dashed line) conductance of the nanocrystal-based MIS diodes.

an image charge on the metal is formed,[15] which, in turn, reduces E_c. Thus, our value of 210 meV for E_c is consistent with our device. The fitted position of the CB is a few tenths of a volt higher in energy than expected for an ideal 38 Å CdSe particle. Similar discrepancies have been reported for bulk semiconductors.[16] Ionized surface states as well as the dielectric medium surrounding the particle can modify the local fields around a particle.[7]

By comparing the measured versus the modeled conductance, we can try to understand the physics of the device. Between 0.4 and 0.7 V the measured conductance increases slightly. This is a small effect and probably arises from surface states in the CdSe NCs. We assign the feature between 0.7 and 0.9 V to be the contribution from the first charging state. The differences in voltages between the higher discontinuity points were measured to be ~200 meV, indicating that those states correspond to higher single-electron charging states. The diode behavior originates from the same physics that characterize a bulk MIS diode. Two distinct tunneling processes, each occurring at different applied voltages, describe the reverse and forward bias cases: from the CdSe VB to the metal, and from the metal to the CdSe CB.

These diodes are similar to resonant tunneling diodes (RTDs),[17] but are not characterized by regions of negative conductance. This is because the resonant states are dominated by Coulombic charging states, rather than the discrete electronic structure of the CdSe CB. It is possible that with a sufficiently narrow distribution of smaller NCs, a RTD with negative differential conductance could be fabricated using the approach described here.

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[1] V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature (London) **370**, 354 (1994).
[2] N. C. Greenham, X. Peng, and A. P. Alivisatos, Phys. Rev. B **54**, 17628 (1996).
[3] G. Markovich, D. V. Leff, S.-W. Chung, H. Soyez, B. Dunn, and J. R. Heath, Appl. Phys. Lett. **70**, 3107 (1997).
[4] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, and P. L. McEuen, Nature (London) **389**, 699 (1997).
[5] B. Alperson, S. Cohen, I. Rubinstein, and G. Hodes, Phys. Rev. B **52**, 17017 (1995).
[6] C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones, and J. M. Tour, Appl. Phys. Lett. **71**, 611 (1997).
[7] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
[8] B. O. Dabbousi, C. B. Murray, M. F. Rubner, and M. G. Bawendi, Chem. Mater. **6**, 216 (1994).
[9] S. Roth, S. Blumentritt, M. Burghard, C. Fisher, G. Philipp, and C. Müller-Schwanneke, Synth. Met. **86**, 2415 (1997).
[10] M. Iwamoto, M. Wada, and T. Kubota, Thin Solid Films **243**, 472 (1994).
[11] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[12] T. C. Chiang and F. J. Himpsel, Landolt-Börnstein, New Series III/23a, 95 (1989).
[13] L. E. Brus, J. Chem. Phys. **79**, 2745 (1996).
[14] M. Ammam, R. Wilkins, E. Ben-Jacob, P. Maker, and R. Jaklevic, Phys. Rev. B **43**, 1146 (1991).
[15] P. Lorrain and D. R. Corson, *Electromagnetic Fields and Waves* (1970), p. 150.
[16] H. C. Card and E. H. Rhoderick, J. Phys. D **4**, 1589 (1971).
[17] T. Schmidt, R. J. Haug, K. VonKlitzing, and A. Forster, Phys. Rev. B **55**, 2230 (1997).